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NONADIABATIC THEORY OF ELECTRON-HYDROGEN SCATTERING, PART II

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SUMMARY

The triplet S-wave electron-atomic hydrogen elastic scattering phase shifts are recalculated by a previously introduced nonadiabatic theory. The previous calculation has been improved in a number of respects, the most important of which is the use of a noniterative technique for numerically solving the partial differential equations. (This technique is expected to be useful for a large class of linear second order elliptic partial differential equations.) Phase shifts are computed to better than four significant figures. The results are quite close to the variational results of Schwartz but on the whole somewhat larger. The deviations are considered significant, and the various approaches are discussed: Specifically our triplet scattering length (in Bohr radii) is $a_t = 1.7683$.

CONTENTS

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INTRODUCTION

The extension of the relative partial wave treatment to the (electron-hydrogen) scattering problem was introduced (Reference 1) to allow for the calculation of phase shifts of sufficient accuracy for experimental purposes and to allow for meaningful comparison by approximate theories. The completion of the original program (Reference 2) has apparently met the purposes for which it was intended (Reference 3). Reference 2 will be referred to here as Part I, and equations in it which are referred to will be prefixed by a I. This includes any minor variations in notation.

With regard to the original calculation, it was clear from the first that the devices introduced to elicit information about the higher corrections — which, precisely speaking, involved the solutions of two-dimensional partial differential equations — limited the accuracy to significantly less than that to which the method was intrinsically capable. In addition, a variational calculation (Reference 4) has appeared in which the estimated accuracy was much higher than in Reference 2.

The variational calculation employed (in Kohn's variational principle) a Hylleraas-type wave function with an increasingly large number N of parameters. The estimate of the error was based on the device, first exploited by Pekeris (Reference 5), of observing the results as a function of N. However, for at least two reasons, the variational calculations pertaining to scattering are not compelling to the accuracy claimed. First, the variational results at non-zero energies show, as a function of the nonlinear parameter, a kind of wild behavior which has required a very intuitive method of interpretation (Reference 6). (For $k > 0$ we do not have the cushion of a guaranteed lower bound on the phase shifts.) More important, however, is the fact that a Hylleraas wave function does not naturally describe the complete wave function corresponding to a scattering problem. In fact, it has been conclusively demonstrated (Reference 7) that at zero energy the long-range adiabatic tail is essential for highly quantitative purposes. Although the variational calculation finally did include such a term at zero energy, it did not include it for non-zero energies; it is still very much in question to what extent this term enters at small but finite energies.

*With the exception of the description of the numerical method of solution appearing on pages 8 through 14 this paper has been published in *Phys. Rev.* 129(3):1250-1257, February 1963.

For these reasons it has seemed necessary to carry out our intention of numerical integration for the higher order correction. The calculation has been restricted to the triplet case as discussed in the next section. In the third section of this paper we discuss the method of numerically integrating the partial differential equations. Finally in the fourth section of this paper we present results and discussion.

REVIEW OF THE NONADIABATIC THEORY

It will be recalled that the nonadiabatic theory (Reference 2) starts with a decomposition of the S-wave function

$$\Psi\left(r_1 r_2 \theta_{12}\right) = \frac{1}{r_1 r_2} \sum_{l=0}^{\infty} \sqrt{2l+1}\, \Phi_l\left(r_1 r_2\right) P_l\left(\cos\theta_{12}\right), \tag{I-3}$$

from which by substitution into the Schrodinger equation an infinite set of coupled two-dimensional partial differential equations (Equations I-4) results. We define a zeroth order problem by neglecting the coupling terms of the $l = 0$ equation; thus

$$\left(\Delta_{12} + E + \frac{2}{r_2}\right) \Phi_0^{(0)}\left(r_1 r_2\right) = 0, \tag{I-11}$$

where

$$\Delta_{12} \equiv \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}.$$

The zeroth order wave function $\Phi_0^{(0)}$ is required to have the asymptotic boundary condition corresponding to a scattered wave:

$$\lim_{r_1 \to \infty} \Phi_0^{(0)}\left(r_1 r_2\right) = \sin\left(k r_1 + \delta_0\right) R_{1s}\left(r_2\right), \tag{I-12}$$

where δ_0 is the zeroth-order phase shift, and δ_0 can be interpreted as the phase shift of a rudimentary type of three-body problem, to which, it has been shown in Reference 2, many previous approximations were unknowingly addressed.

The basic relation of the nonadiabatic theory is given by

$$\sin\left(\delta - \delta_0\right) = -\frac{1}{k} \sum_{l=1}^{\infty} \frac{2}{\sqrt{2l+1}} \int_0^{\infty} dr_1 \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^{\,l}}{r_1^{\,l+1}} \Phi_l\, dr_2, \tag{I-13}$$

where δ is the exact S-wave phase shift. The integration domain is confined to the region $r_1 \geq r_2$. The convergence of the terms on the right-hand side was established by noting that the significant contribution to each integral comes from two regions. One is the adiabatic region, $r_1 >> r_2$ and r_2 small. We shall have much to say about this contribution in connection with the shortcomings of the Hylleraas wave function variational approach; however, for the purposes of the present nonadiabatic theory these contributions can readily be accounted for, and can be shown to diminish rapidly as a function of l. The other region which must be considered is for intermediate values of r_1 and r_2; this gives the essential contribution to the deviation of δ from δ_0. A powerful (but nonrigorous) argument for the convergence of this contribution has been given in Reference 2. Briefly it was noted there that each Φ_l equation was a centrifugal barrier term $-l(l+1)\left(r_1^{-2}+r_2^{-2}\right)$ which successively diminishes the amplitude of Φ_l in that region. This argument is the analog of the well known argument that the contributions of successive partial waves go down for low impacting energies in the complete description of the scattering process. It should be emphasized, however, that there is not a one-to-one correspondence in this analogy, for in the equations of partial waves there are no coupled terms, whereas in Equation I-4 the relative partial wave equations are coupled. Thus, whereas we can assert rigorously that only partial S-waves contribute to the zero-energy cross section, it is not true that only the s-relative angular momentum state contributes to the S-wave phase shift at zero energy. What is here being asserted is that the contributions from higher relative angular momentum states diminish in a usefully convergent manner.

There is an additional circumstance, which was not really emphasized in Reference 2, which renders the argument of convergence particularly cogent in the triplet case. In that case we have the boundary conditions

$$\Phi_l\left(r_1 = r_2\right) = 0, \quad l = 0, 1, \cdots$$

$$\Phi_0^{(0)}\left(r_1 = r_2\right) = 0 \cdot \tag{I-6}$$

From inspection of Equation I-13 we can see, by virtue of the r_2^l/r_1^{l+1} factor, that the region $r_2 \gtrsim r_1$ would tend to become increasingly important for the higher relative partial waves. However, because of the boundary condition, the contribution from this region must in fact be small; therefore the main contribution to each integral must come from r_2 significantly less than r_1. But in that region r_2^l/r_1^{l+1} certainly diminishes rapidly as a function of l. Thus, we have every reason for believing the convergence will be exceedingly rapid in the triplet case. The same arguments should also render our perturbation theory

$$\Phi_l = \sum_{j=0}^{\infty} \lambda^{j+l/2}\, \Phi_l^{(j)}$$

particularly effective.

These reasons plus the calculated values which are presented below give a strong expectation that when the terms through quadratic order are included in the calculation, more than four-place accuracy will be obtained in the phase shifts. This accuracy is required if the results are to be compared meaningfully with Schwartz's results.

The original calculation (Reference 2) has been improved in two main respects. Firstly we have generalized the zeroth order technique of solution to double precision arithmetic on the IBM 7090 computer. In the single precision program we were plagued with vanishing determinants which very rapidly used up all the eight significant figures that the machine could store. In the double precision program, the 16 significant figures were sufficient to yield zeroth order phase shifts from better than four to almost eight significant figures.

To illustrate the gain in accuracy of our zeroth order results by making the program double precision, Table 1 presents a typical set of results for $k = 0.2$. The middle two columns refer to quantities labeled det and I_T in Reference 2. From the first of these we can obtain an indication of the number of significant figures lost in the evaluation of the determinant det. For example, in the row corresponding to the expansion 2, 3, 4, and 5, the main diagonal of det, that is, $\prod_{i=1}^{4} (ME)_{ii}$, is approximately 0.6×10^{-9}, if we figure 0.5×10^{-2} as the average value of a diagonal matrix element. Comparing this value with 0.42×10^{-25}, the actual value of the determinant, we see that approximately 16 significant figures have been lost;* this is the maximum number of significant figures that the double precision arithmetic affords, and the conclusion is reinforced by referring to the next row, 2, 3, 4, 5, I_0. Here almost 25 significant figures have been lost, and the corresponding diagonal sum increases! If the elements of the calculation have sufficient (infinite) accuracy, it is clear that the addition of a term to an expansion can only decrease the diagonal sum. Thus, the δ_0 for that expansion is very unreliable. In each of the groups of rows separated by dotted lines each subsequent row augments the previous one by an additional term. It should be noted that except for the above case the diagonal sums diminish. This should be compared with Table 3 of Reference 8 in which a similar set of results based on a single precision program was presented. There an increase in the diagonal sum occurred in third row! In the present case, we could with some legitimacy claim $\delta_0 = 2.6794194(3)$; however the value $\delta_0 = 2.67942$ is quite adequate for our purposes.

Table 1

Zeroth Order Double Precision Results for k = 0.2.

Expansion	Determinant	Diagonal Sum	δ_0
2	0.154×10^{-1}	0.358×10^{-2}	2.71098
2,3	0.315×10^{-6}	0.141×10^{-4}	2.679565
2,3,4	0.541×10^{-14}	0.231×10^{-6}	2.6794215
2,3,4,5	0.418×10^{-25}	0.137×10^{-8}	2.6794197
2,3,4,5,I_0	0.246×10^{-36}	0.553×10^{-7}	2.67962
. . . . .	. . . . .	. . . . .	. . . . .
2,3,I_0	0.621×10^{-12}	0.823×10^{-7}	2.6794200
2,3,I_0,I_1	0.329×10^{-16}	0.142×10^{-7}	2.6794192
. . . . .	. . . . .	. . . . .	. . . . .
2,4,I_0	0.123×10^{-12}	0.773×10^{-8}	2.6794191
2,4,I_0,I_5,I_{10},I_{20}	0.638×10^{-26}	0.742×10^{-8}	2.6794191

*The formula for tan 2δ involves, among other things, the value of the determinant. It does not follow, however, that there is a one-to-one correspondence between the number of significant figures in the determinant and in tan 2δ. We have inferred the number of significant figures by the uniformity of the results for δ as shown in Table 1. The details are discussed further in Reference 8.

The second and main advancement we have achieved in the way of computing the complete S-wave phase shifts is the numerical integration of the higher order equations. These are elliptic equations, and it is well known that the usual way of numerically solving an elliptic equation is by some sort of relaxation of iteration technique. The novel feature of the technique we have used is that it is not iterative. Because it has worked where a relaxation technique has utterly failed to converge, and because it is applicable to a whole class of linear second-order equations, we have given some detail in the next section to the numerical solution.

SOLUTION OF THE PARTIAL DIFFERENTIAL EQUATIONS

The higher order effects in our expansion are given by the formula

$$\sin\left(\delta - \delta_0\right) = -\frac{1}{k}\sum_{\nu=1}^{\infty}\lambda^{\nu}\sum_{\substack{m+\mu=\nu \\ m\geq 1,\ \mu\geq 0}}\frac{2}{\sqrt{2m+1}}\int_0^{\infty}\int_0^{r_1}\Phi_0^{(0)}\,\frac{r_2^{m}}{r_1^{m+1}}\,\Phi_m^{(\mu)}\,dr_1\,dr_2 \tag{I-43}$$

(For the purposes of the discussion in the fourth section of this paper we emphasize that this λ-expansion is a modification of the ordinary l-expansion in relative partial waves, which is expected to hasten the convergence in the triplet case. It also has additional advantages discussed in Reference 2.)

The partial differential equation for $\Phi_0^{(0)}$ has been repeated in the last section. We repeat here the remaining equations:

$$\left[\Delta_{12} - \frac{2}{r_1^2 + r_2^2} + \frac{2}{r_2} + E\right]\Phi_1^{(0)} = \frac{2}{\sqrt{3}}\,\frac{r_2}{r_1^2}\,\Phi_0^{(0)}\,, \tag{I-39}$$

$$\left[\Delta_{12} + \frac{2}{r_2} + E\right]\Phi_0^{(1)} = \frac{2}{\sqrt{3}}\,\frac{r_2}{r_1^2}\,\Phi_1^{(0)}\,, \tag{I-40}$$

$$\left[\Delta_{12} - \frac{6}{r_1^2 + r_2^2} + \frac{2}{r_2} + E\right]\Phi_2^{(0)} = \frac{2}{\sqrt{5}}\,\frac{r_2^2}{r_1^3}\,\Phi_0^{(0)}\,, \tag{I-41}$$

$$\left[\Delta_{12} - \frac{2}{r_1^2 + r_2^2} + \frac{2}{r_2} + E\right]\Phi_1^{(1)} - \frac{4}{5}\,\frac{r_2^2}{r_1^3}\,\Phi_1^{(0)} = \frac{2}{\sqrt{3}}\,\frac{r_2}{r_1^2}\,\Phi_0^{(1)} + \frac{4}{\sqrt{15}}\,\frac{r_2}{r_1^2}\,\Phi_2^{(0)}\,. \tag{I-42}$$

In principle these equations are to be integrated over the infinite region $0 \leq r_2 \leq r_1 < \infty$. In practice, of course, we can only integrate up to a finite point $r_1 = R$. If R is suitably large, we can perform the quadratures in Equation I-43 from R to ∞ by replacing the functions by their adiabatic forms:

$$\Phi_0^{(0)} \approx \sin\left(kr_1 + \delta_0\right) R_{1s}\left(r_2\right)\,, \tag{I-17}$$

$$\Phi_l^{(0)} \approx -\frac{2\sin\left(kr_1 + \delta_0\right)}{r_1^{l+1}\sqrt{2l+1}}\left(e^{-r_2}\right)\left(\frac{r_2^{l+2}}{l+1} + \frac{r_2^{l+1}}{l}\right), \qquad l = 1, 2 \tag{I-47}$$

$$\Phi_1^{(1)} \approx -\frac{2}{\sqrt{3}}(\Delta\delta_0)\frac{\cos(kr_1+\delta_0)}{r_1^2}\left(e^{-r_2}\right)\left(\frac{r_2^3}{2}+r_2^2\right). \tag{I-48}$$

(These functions are exact solutions in the limit $r_1 \to \infty$.)

The δ_0 being known, these equations with $r_1 = R$ then define the boundary conditions on the numerical solution in the region $0 \leq r_2 \leq r_1 \leq R$. It must be emphasized that as long as R is finite there is an approximation involved in these equations as boundary conditions. For these forms require not only $R \to \infty$, but also that $r_2 << R$. However, for numerical purposes we must know the boundary conditions for all values of $r_2 \leq R$; the most natural thing to do is simply to use the above equations for all values of r_2. If R is large enough, we can be sure that the error thus incurred is very small, because in the region $r_2 \gtrsim R$ both the above functions and the true functions will be negligibly small.

The important question concerning R is, how large is large enough? The time required for numerical integration effectively limited us to an R = 10. It was our original intention to use the numerically integrated $\Phi_0^{(0)}$ in the quadratures (Equation I-43) together with the remaining numerically integrated functions. Our suspicion of the accuracy of the numerically integrated function was aroused when at k = 0.4 we found that

$$\int_0^R \int_0^{r_1} \frac{r_2}{r_1^2}\left(\Phi_0^{(0)}\right)^2 dr_1\, dr_2$$

was half the value that we had gotten using the analytic expansion of $\Phi_0^{(0)}$ that we had as a by-product of the calculation of δ_0. We were therefore led to examine the deviation of our original $\Phi_0^{(0)}$

$$\Phi_0^{(0)} = \sin(kr_1+\delta_0)\, R_{1s}(r_2) + \left(\sum_n + \int dp\right) C_n e^{-\kappa_n r_1} R_{ns}(r_2) \tag{I-19}$$

from the boundary values imposed on the numerical solution by Equation I-17. The results are given in Table 2.

Table 2

Comparison of the Numerically Integrated Boundary Values at $r_1 = 10$ (k = 0.4) with the Expansion of $\Phi_0^{(0)}$ in Equation I-19.

r_2	$\Phi_0^{(0)}(10, r_2)$	$\sin(10k+\delta_0)\, R_{1s}(r_2)$
1	-0.01913	-0.01853
2	-0.01363	-0.01363
3	-0.00685	-0.00752
4	-0.00259	-0.00369
5	-0.00042	-0.00170
6	0.000486	-0.000749
7	0.000722	-0.000321
8	0.000612	-0.000135
9	0.000334	-0.0000056
10	-0.000003	0[a]

[a]The expression on the left is not 0 at this point; however, for the purposes of numerical integration this point, being equal to r_1 at r_2, it was automatically taken as 0 by our program.

The important thing to notice is that the values obtained from the analytic $\Phi_0^{(0)}$ along the line $r_1 = 10$ change sign at $r_2 \approx 5$ whereas those defined by Equation I-17, being proportional to $R_{1s} = 2r_2 e^{-r_2}$, do not. We concluded that this change of sign which was not taken care of in the boundary condition of Equation I-17 was responsible for the inaccuracy of the numerically integrated $\Phi_0^{(0)}$.

The double integral in which we observed the discrepancy is of course part of the dipole "sum rule"

$$\int_0^\infty \int_0^{r_1} \Phi_0^{(0)} \left[-2 \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \right] \Phi_1^{(0)} \, dr_1 \, dr_2 = \frac{2}{\sqrt{3}} \int_0^\infty \int_0^{r_1} \left(\Phi_0^{(0)} \right)^2 \frac{r_2}{r_1^2} \, dr_1 \, dr_2 \, . \qquad \text{(I-51)}$$

In the original calculation (Reference 2) we used this relation to find the nonadiabatic effects of $\Phi_1^{(0)}$. In the present case, Equation I-51 together with its counterpart for $\Phi_2^{(0)}$, plus additional sum rules that we can derive, serve as a check of the numerical integration. Now in the above noted $k = 0.4$ case it was observed that the $\Phi_1^{(0)}$ found from Equation I-39 using the numerically integrated (incorrect) $\Phi_0^{(0)}$ gave approximate equality in the sum rule. At work here was undoubtedly the phenomenon that the (incorrect) $\Phi_0^{(0)}$ is an important enough inhomogeneous term in the differential equation to influence $\Phi_1^{(0)}$ to be incorrect in just such a way as to give equality in Equation I-51. This experience prevented any complacency on our part that the satisfaction of sum rules of the numerical function was a foolproof guarantee that the functions were correct.

The $k = 0.4$ case is extreme in the sense that at no other energy have we observed the analytic $\Phi_0^{(0)}$ to change sign in such a prominent place along the boundary. (The change apparently stems from the fact that $\Phi_0^{(0)}$ has a node very close to $r_1 = 10$ at this energy.) Accordingly the differences between the integrals on the right-hand side of Equation I-51 using the numerical versus the analytic $\Phi_0^{(0)}$ at other energies differed only in the second significant figure. However, since we require practically three significant figures in the integral

$$\Delta\delta_0 = -\frac{1}{k} \left(\int_0^{10} \int_0^{r_1} \Phi_0^{(0)} \frac{r_2}{r_1^2} \Phi_1^{(0)} \, dr_1 \, dr_2 + \int_{10}^\infty \int_0^{r_1} \Phi_0^{(0)} \frac{r_2}{r_1^2} \Phi_1^{(0)} \, dr_1 \, dr_2 \right) \qquad \text{(I-44)}$$

we could not use the numerically integrated $\Phi_0^{(0)}$.

We therefore decided to use the $\Phi_0^{(0)}$ obtained from the best expansion (Equation I-19) we had and numerically integrate for the remaining functions. Our unfortunate experience with the dipole sum rule gave us some confidence that having a reliable $\Phi_0^{(0)}$ would make up for any deficiencies in the boundary conditions for the other functions. The sum rules, of course, still are a necessary condition to be satisfied; however, in view of the necessity of cutting off the numerical integrals at R, the sum rules did not afford a critical test of the accuracy. We found that we did have to go a mesh size $h = 0.1$ to get reasonable results. The most natural further tests of accuracy—further halving the mesh size, integrating out to double the value of R etc.—were precluded by machine storage and particularly time considerations. As it was, it took 90 minutes to integrate a differential equation on the IBM 7090, so that at nine energies and five equations per energy, we had already used a vast amount of time. As we

have said, we are quite confident that we have attained a requisite accuracy, but our present inability to carry out further checks provides the most serious weakness in the present calculation. We hope to carry through some of these checks as bigger and faster computers become available.

We now turn to the problem of numerically integrating the partial differential equations. In the most general case, we have the following boundary value problem: $\phi(x,y)$ satisfies Equation 1 in a domain $\mathcal{D}$

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + g(x,y)\,\phi = f(x,y) , \tag{1}$$

where the values of ϕ on the boundary are known. If we replace the second order partial derivatives in Equation 1 with the second differences

$$\frac{\partial^2 \phi}{\partial x^2} \cong \frac{1}{h^2}\left[\phi(x+h,y) - 2\phi(x,y) + \phi(x-h,y)\right] ,$$

$$\frac{\partial^2 \phi}{\partial y^2} \cong \frac{1}{h^2}\left[\phi(x,y+h) - 2\phi(x,y) + \phi(x,y-h)\right] ,$$

then Equation 1 can be written as

$$\phi(x+h,y) + \phi(x-h,y) + \phi(x,y+h) + \phi(x,y-h) + \left[h^2 g(x,y) - 4\right]\phi(x,y) = h^2 f(x,y) .$$

(The method we shall subsequently present is readily extendable to higher order difference formulas.) When this is done we have reduced the problem to a solution of the matrix equation

$$A\phi = k , \tag{2}$$

with A an $N2 \times N2$ non-singular, real matrix of the coefficients of ϕ at the N2 internal mesh points and k a known column vector of the boundary values.

The N2 being on the order of the square of the number of mesh points along a boundary N, it appears that a direct inversion of Equation 2 would be almost impossible. For that reason an iterative solution is usually attempted in which A is written

$$A = I - B ,$$

where I is the unit matrix.

The iteration procedure is defined by

$$\phi^{(n+1)} = B\phi^{(n)} + k . \tag{3}$$

The superscripts refer to the iteration number. The $\phi^{(0)}$ is an initial arbitrary guess of the solution. If we define λ_i, $i = 1, n$ to be the eigenvalues of matrix B, then

$$\lambda_{max} = \max_{1 \leq i \leq n} |\lambda_i| .$$

A necessary and sufficient condition for the convergence of system of Equation 3 is that $\lambda_{max} < 1$ (Reference 9).

The iterative techniques used in the solution of matrix equations are applicable to a wide class of boundary value problems, but it is sometimes very difficult to determine whether λ_{max} is less than one. If λ_{max} is less than but close to one, the number of iterations required for a satisfactory solution becomes quite large.

The following is an exact method of solving the matrix problem defined by Equation 1. In essence we are exploiting the fact that although A is of gigantic dimension, it is of a special form, and most of its elements are zero.

The matrix A of Equation 2 is of the form:

$$A = \begin{bmatrix} A_{1,1} & A_{1,2} & 0 & \cdots & & & & & & & & & \\ A_{2,1} & A_{2,2} & A_{2,3} & 0 & \cdots & & & & & & & & \\ 0 & A_{3,2} & A_{3,3} & A_{3,4} & 0 & \cdots & & & & & & & \\ \cdots & & & & & & & & & & & & \\ \cdots & 0 & A_{N-2,N-3} & A_{N-2,N-2} & A_{N-2,N-1} & 0 & & & & & & & \\ \cdots & 0 & A_{N-1,N-2} & A_{N-1,N-1} & A_{N-1,N} & & & & & & & & \\ \cdots & 0 & A_{N,N-1} & A_{N,N} & & & & & & & & & \end{bmatrix}$$

where for the particular triangular boundary of the zeroth order problem $A_{1,1}$ is of dimension $N \times N$; $A_{1,2}$ of $N \times (N-1)$; $A_{2,1}$ of $(N-1) \times N$; $A_{2,2}$ of $(N-1) \times (N-1)$; $\cdots\cdots\cdots$ $A_{N,N-1}$ of 1×2 and $A_{N,N}$ of 1×1

We now factor matrix A into the product of two matrices

$$A = LU ,$$

which in terms of block matrices can be written:

$$\begin{bmatrix} A_{1,1} & A_{1,2} & 0 & \cdots & & & & & & & & & \\ A_{2,1} & A_{2,2} & A_{2,3} & 0 & \cdots & & & & & & & & \\ 0 & A_{3,2} & A_{3,3} & A_{3,4} & 0 & \cdots & & & & & & & \\ \cdots & & & & & & & & & & & & \\ \cdots & 0 & A_{N-2,N-3} & A_{N-2,N-2} & A_{N-2,N-1} & 0 & & & & & & & \\ \cdots & 0 & A_{N-1,N-2} & A_{N-1,N-1} & A_{N-1,N} & & & & & & & & \\ \cdots & 0 & A_{N,N-1} & A_{N,N} & & & & & & & & & \end{bmatrix} = \begin{bmatrix} L_{1,1} & & & & & & & & & & & & \\ L_{2,1} & L_{2,2} & & & & & & & & & & & \\ 0 & L_{3,2} & L_{3,3} & & & & & & & & & & \\ \cdots & & & & & & & & & & & & \\ & & 0 & L_{N-2,N-3} & L_{N-2,N-2} & & & & & & & & \\ & & & 0 & L_{N-1,N-2} & L_{N-1,N-1} & & & & & & & \\ & & & & 0 & L_{N,N-1} & L_{N,N} & & & & & & \end{bmatrix} \begin{bmatrix} I & U_{1,2} & 0 & \cdots & & & & & & & & & \\ & I & U_{2,3} & 0 & \cdots & & & & & & & & \\ & & I & U_{3,4} & 0 & \cdots & & & & & & & \\ & & & & & & & & & & & & \\ & & & & I & U_{N-2,N-1} & 0 & & & & & & \\ & & & & & I & U_{N-1,N} & & & & & & \\ & & & & & & I & & & & & & \end{bmatrix} \quad (4)$$

Performing the multiplication of L by U as defined by Equation 4 we can express $L_{i,j}, U_{i,j}$ $i,j = 1,N$ in terms of the given matrix A.

$$\begin{aligned} L_{1,1} &= A_{1,1} \\ L_{i,i-1} &= A_{i,i-1} \qquad i = 2,N \\ U_{i-1,i} &= L^{-1}_{i-1,i-1} A_{i-1,i} \qquad i = 2,N \\ L_{i,i} &= A_{i,i} - L_{i,i-1} U_{i-1,i} \qquad i = 2,N. \end{aligned} \tag{5}$$

The factorization of A in the form of Equation 4 is only possible if the matrices $L_{i,i}$, $i = 1,N$ are nonsingular (Reference 10).

With this factorization, we have from Equation 2

$$A\phi = LU\phi = k . \tag{6}$$

We let $U\phi = \zeta$, and this gives from Equation 6

$$L\zeta = k , \tag{7}$$

$$\zeta = L^{-1}k . \tag{8}$$

Writing Equation 7 more explicitly, we have in terms of the block matrices of L

$$\begin{bmatrix} L_{1,1} & & & & & & \\ L_{2,1} & L_{2,2} & & & & & \\ 0 & L_{3,2} & L_{3,3} & & & & \\ \cdot & \cdot & \cdot & \cdot & & & \\ & 0 & L_{N-2,N-3} & L_{N-2,N-2} & & & \\ & & 0 & L_{N-1,N-2} & L_{N-1,N-1} & & \\ & & & 0 & L_{N,N-1} & L_{N,N} \end{bmatrix} \begin{bmatrix} \bar{\zeta}_1 \\ \bar{\zeta}_2 \\ \bar{\zeta}_3 \\ \cdot \\ \cdot \\ \cdot \\ \bar{\zeta}_N \end{bmatrix} = \begin{bmatrix} \bar{k}_1 \\ \bar{k}_2 \\ \bar{k}_3 \\ \cdot \\ \cdot \\ \cdot \\ \bar{k}_N \end{bmatrix} \tag{9}$$

where $\bar{\zeta}_1$, $\bar{k}_1$ are vectors of N elements, $\bar{\zeta}_2$, $\bar{k}_2$ are vectors of $(N-1)$ elements, ..., $\bar{\zeta}_N$, $\bar{k}_N$ are vectors of 1 element.

From Equation 9:

$$\begin{aligned} \bar{\zeta}_1 &= L^{-1}_{1,1} \bar{k}_1 , \\ \bar{\zeta}_i &= L^{-1}_{i,i} \left(\bar{k}_i - L_{i,i-1} \bar{\zeta}_{i-1} \right) \qquad i = 2,N . \end{aligned} \tag{10}$$

We have

$$U\phi = \zeta \,, \tag{11}$$

and putting this in more explicit form, we have

$$\begin{bmatrix} I & U_{1,2} & 0 & \cdots & & & \\ & I & U_{2,3} & 0 & \cdots & & \\ & & I & U_{3,4} & 0 & \cdots & \\ & & & \cdots & & & \\ & & & I & U_{N-2,N-1} & 0 & \\ & & & & I & U_{N-1,N} & \\ & & & & & I & \end{bmatrix} \begin{bmatrix} \bar{\phi}_1 \\ \bar{\phi}_2 \\ \bar{\phi}_3 \\ \cdot \\ \cdot \\ \cdot \\ \bar{\phi}_N \end{bmatrix} = \begin{bmatrix} \bar{\zeta}_1 \\ \bar{\zeta}_2 \\ \bar{\zeta}_3 \\ \cdot \\ \cdot \\ \cdot \\ \bar{\zeta}_N \end{bmatrix} \tag{12}$$

From Equation 12 we obtain

$$\bar{\phi}_N = \bar{\zeta}_N \,,$$

$$\bar{\phi}_{i-1} = \bar{\zeta}_{i-1} - U_{i-1,i} \cdot \bar{\phi}_i \qquad i = 2, N \,. \tag{13}$$

An examination of Equations 10 and 13 indicates that the only inversions necessary in the entire computation are the inversions of the matrices $L_{i,i}$ $i = 1,N$. This is a result of our factorization which places the identity matrix on the block diagonal matrices of U. It is of the essence that the matrices $L_{i,1}$ are, in practice, of a much smaller dimension than the original matrix. For the particular boundary we are considering (see also, Figure 1 of Reference 2) the dimension of $L_{i,i}$ decreases from $L_{N,N}$ (an $N \times N$ matrix) to $L_{1,1}$ (dimension 1×1).

We now give an example of the numerical method discussed above. Suppose we wish to solve the following boundary value problem in the domain $\mathfrak{D}$:

$$\frac{\partial^2}{\partial x^2}\phi(x,y) + \frac{\partial^2}{\partial y^2}\phi(x,y) + \left(\frac{2}{y} - 6x - 1\right)\phi(x,y) = \frac{xe^{-x}}{36} \,. \tag{14}$$

We wish to determine the interior points $\phi_1, \phi_2, \phi_3, \ldots, \phi_{10}$ with the boundary values as specified in Figure 1. The problem is reduced

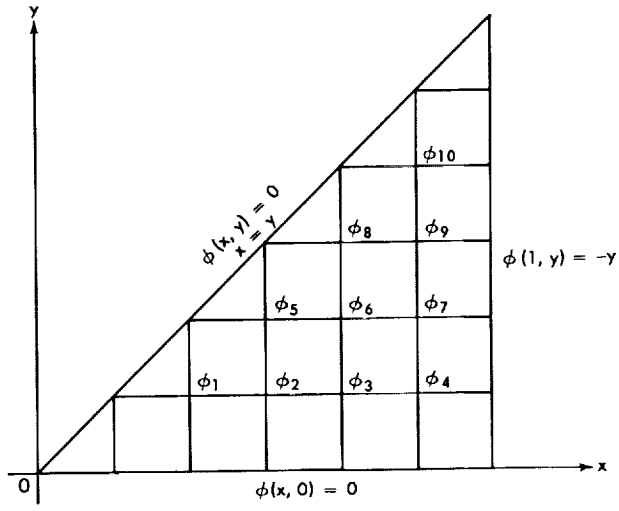

Figure 1—The domain of integration ($\mathfrak{D}$) of the example given in Equation 14.

to a solution of the following system of equations:

$$
\begin{aligned}
\tfrac{135}{36}\phi_1 + \phi_2 &= \tfrac{1}{3}e^{-1/3},\\
\phi_1 - \tfrac{136}{36}\phi_2 + \phi_3 + \phi_5 &= \tfrac{1}{2}e^{-1/2},\\
\phi_2 - \tfrac{137}{36}\phi_3 + \phi_4 + \phi_6 &= \tfrac{2}{3}e^{-2/3},\\
\phi_3 - \tfrac{138}{36}\phi_4 + \phi_7 &= \tfrac{1}{6} + \tfrac{5}{6}e^{-5/6},\\
\phi_2 - \tfrac{142}{36}\phi_5 + \phi_6 &= \tfrac{1}{2}e^{-1/2},\\
\phi_3 + \phi_5 - \tfrac{143}{36}\phi_6 + \phi_7 &= \tfrac{2}{3}e^{-2/3},\\
\phi_4 + \phi_6 - \tfrac{144}{36}\phi_7 &= \tfrac{1}{3} + \tfrac{5}{6}e^{-5/6},\\
\phi_6 - \tfrac{145}{36}\phi_8 + \phi_9 &= \tfrac{2}{3}e^{-2/3},\\
\phi_7 + \phi_8 - \tfrac{146}{36}\phi_9 + \phi_{10} &= \tfrac{1}{2} + \tfrac{5}{6}e^{-5/6},\\
\phi_9 - \tfrac{147}{36}\phi_{10} &= \tfrac{2}{3} + \tfrac{5}{6}e^{-5/6},
\end{aligned}
$$

where $\phi_1, \phi_2, \phi_3, \ldots, \phi_{10}$ are values of the function at the interior points.

The preceding system of equations written in matrix form gives

$$
\begin{bmatrix}
-\frac{135}{36} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & -\frac{136}{36} & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & -\frac{137}{36} & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & -\frac{138}{36} & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & -\frac{142}{36} & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & -\frac{143}{36} & 1 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & -\frac{144}{36} & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & -\frac{145}{36} & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & -\frac{146}{36} & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -\frac{147}{36}
\end{bmatrix}
\begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \\ \phi_5 \\ \phi_6 \\ \phi_7 \\ \phi_8 \\ \phi_9 \\ \phi_{10} \end{bmatrix}
=
\begin{bmatrix}
\frac{1}{3}e^{-1/3} \\
\frac{1}{2}e^{-1/2} \\
\frac{2}{3}e^{-2/3} \\
\frac{1}{6}+\frac{5}{6}e^{-5/6} \\
\frac{1}{2}e^{-1/2} \\
\frac{2}{3}e^{-2/3} \\
\frac{1}{3}+\frac{5}{6}e^{-5/6} \\
\frac{2}{3}e^{-2/3} \\
\frac{1}{2}+\frac{5}{6}e^{-5/6} \\
\frac{2}{3}+\frac{5}{6}e^{-5/6}
\end{bmatrix}
$$

We now rewrite the matrix on the preceding page in terms of block matrices, and this gives

$$\begin{bmatrix} A_{1,1} & A_{1,2} & 0 & 0 \\ A_{2,1} & A_{2,2} & A_{2,3} & 0 \\ 0 & A_{3,2} & A_{3,3} & A_{3,4} \\ 0 & 0 & A_{4,3} & A_{4,4} \end{bmatrix} \begin{bmatrix} \bar{\phi}_1 \\ \bar{\phi}_2 \\ \bar{\phi}_3 \\ \bar{\phi}_4 \end{bmatrix} = \begin{bmatrix} \bar{k}_1 \\ \bar{k}_2 \\ \bar{k}_3 \\ \bar{k}_4 \end{bmatrix},$$

where

$$\bar{\phi}_1 = \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{bmatrix}, \qquad \bar{\phi}_2 = \begin{bmatrix} \phi_5 \\ \phi_6 \\ \phi_7 \end{bmatrix}, \qquad \bar{\phi}_3 = \begin{bmatrix} \phi_8 \\ \phi_9 \end{bmatrix}, \qquad \bar{\phi}_4 = \begin{bmatrix} \phi_{10} \end{bmatrix},$$

$$\bar{k}_1 = \begin{bmatrix} \frac{e^{-1/3}}{3} \\ \frac{e^{-1/2}}{2} \\ \frac{2}{3} e^{-2/3} \\ \frac{1}{6} + \frac{5}{6} e^{-5/6} \end{bmatrix}, \quad \bar{k}_2 = \begin{bmatrix} \frac{e^{-1/2}}{2} \\ \frac{2}{3} e^{-2/3} \\ \frac{1}{3} + \frac{5}{6} e^{-5/6} \end{bmatrix}, \quad \bar{k}_3 = \begin{bmatrix} \frac{2}{3} e^{-2/3} \\ \frac{1}{2} + \frac{5}{6} e^{-5/6} \end{bmatrix}, \quad \bar{k}_4 = \begin{bmatrix} \frac{2}{3} + \frac{5}{6} e^{-5/6} \end{bmatrix},$$

$$A_{1,1} = \begin{bmatrix} -\frac{135}{36} & 1 & 0 & 0 \\ 1 & -\frac{136}{36} & 1 & 0 \\ 0 & 1 & -\frac{137}{36} & 1 \\ 0 & 0 & 1 & -\frac{138}{36} \end{bmatrix}, \qquad A_{2,2} = \begin{bmatrix} -\frac{142}{36} & 1 & 0 \\ 1 & -\frac{143}{36} & 1 \\ 0 & 1 & -\frac{144}{36} \end{bmatrix},$$

$$A_{3,3} = \begin{bmatrix} -\frac{145}{36} & 1 \\ 1 & -\frac{146}{36} \end{bmatrix}, \qquad A_{4,4} = \begin{bmatrix} -\frac{147}{36} \end{bmatrix}, \qquad A_{2,1} = A_{1,2}^T = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix},$$

$$A_{3,2} = A_{2,3}^T = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad A_{4,3} = A_{3,4}^T = \begin{bmatrix} 0 & 1 \end{bmatrix}.$$

Outlined below is the general form for carrying the computation to completion after the matrices $A_{i,j}$ with $i, j = 1,4$, and the vectors $\bar{k}_i$ with $i = 1,4$ have been formed.

We first invert $A_{1,1} = L_{1,1}$ and multiply $L_{1,1}^{-1}$ by the vector $\bar{k}_1$. This gives the vector $\bar{\zeta}_1$ (Equations 10), which we store because it is used later in the computation of the vectors $\bar{\phi}_i$. We now compute the product $L_{1,1}^{-1} A_{1,2} = U_{1,2}$, which is also stored because it is used in the computation of the vectors $\bar{\phi}_i$. We now multiply $U_{1,2}$ by $L_{2,1} = A_{2,1}$, and subtracting the resulting matrix from $A_{2,2}$, we have $L_{2,2}$, which we invert. The next computation necessary is the product $L_{2,1}\ \bar{\zeta}_1$ and the resulting vector is subtracted from $\bar{k}_2$. We multiply the vector $\left(\bar{k}_2 - L_{2,1}\ \bar{\zeta}_1\right)$ just evaluated by $L_{2,2}^{-1}$, and this gives us the vector $\bar{\zeta}_2$. A repetition of the above operations will finally give us the vectors $\bar{\zeta}_1$, $\bar{\zeta}_2$, $\bar{\zeta}_3$, $\bar{\zeta}_4$, and the matrices $U_{1,2}, U_{2,3}, U_{3,4}$. This completes the first part of the computation. We are now in a position to compute the values of the function ϕ from Equations 13.

From Equation 13, we have $\bar{\phi}_4 = \bar{\zeta}_4$. We form the product $U_{3,4}\bar{\phi}_4$, which we subtract from $\bar{\zeta}_3$ and obtain the vector $\bar{\phi}_3$. Continuing in this manner, we compute finally all the vectors $\bar{\phi}_1$, $\bar{\phi}_2$, $\bar{\phi}_3$, $\bar{\phi}_4$ which are the solution of our boundary value problem.

RESULTS AND DISCUSSION

In Table 3 we have tabulated our results for the higher order corrections. The formula for $\Delta\delta_0$ has been given in the previous section.

Table 3

Resumé of Higher Order Results *

k*	$\Delta\delta_0$ 0-10	$\Delta\delta_0$ 10-∞	$\Delta^2\delta_0^{(2)}$ 0-10	$\Delta^2\delta_0^{(2)}$ 10-∞	$\Delta^2\delta_0^{(1)}$ 0-10	$\Delta^2\delta_0^{(1)}$ 10-∞
0	-0.20256	-0.3526	-0.012304	-0.00322	-0.001032	-0.00822
0.1	0.01895	0.01049	0.001168	0.000199	0.000369	0.000129
0.2	0.03136	0.00510	0.002016	0.000119	-0.000325	-0.000052
0.3	0.03530	0.00166	0.002418	0.000029	-0.00132	-0.000021
0.4	0.03373	0.00159	0.0024685	0.000026	-0.00228	+0.000019
0.5	0.03129	0.00188	0.002384	0.000041	-0.00140	0.0000049
0.6	0.02939	0.00131	0.002263	0.000028	-0.00141	-0.00000875
0.7	0.02766	0.00085	0.002145	0.000015	-0.00132	-0.0000003
0.8	0.02605	0.00096	0.002047	0.000019	-0.00130	-0.0000045

*For the purposes of the scattering length, the k = 0 entries are negative.

The remaining two integrals are

$$\Delta^2 \delta_0^{(2)} = -\frac{2}{k\sqrt{5}}\left(\int_0^R \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^2}{r_1^3} \Phi_2^{(0)}\, dr_1\, dr_2 + \int_R^\infty \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^2}{r_1^3} \Phi_2^{(0)}\, dr_1\, dr_2\right), \qquad \text{(I-45)}$$

$$\Delta^2 \delta_1^{(1)} = -\frac{2}{k\sqrt{3}}\left(\int_0^R \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^2}{r_1^3} \Phi_1^{(1)}\, dr_1\, dr_2 + \int_R^\infty \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^2}{r_1^3} \Phi_1^{(1)}\, dr_1\, dr_2\right). \qquad \text{(I-43)}$$

The significance of the break-up of the integrals at $R = 10$ has also been explained. In this connection it can hardly be overstressed that for small k a significant contribution comes from the region $R \leq r_1 \leq \infty$.

In Table 4 we have collected results to show the convergence of the terms multiplying successive powers of λ in the nonadabiatic series (see also, Equation 43 in Reference 2). The convergence appears to be even more rapid than an order of magnitude per power of λ. In second order this is due to a partial cancellation of the terms multiplying λ^2, a circumstance which may very well have an increasingly important effect for high powers of λ due to the increasing number of terms which enter. (It is also possible that it might have the opposite effect.) The final δ in each row is then the sum of the entries to its left to the accuracy that we believe it is meaningful. As a simple extrapolation of the convergence, we take this to mean an uncertainty of five units in the last figure given for the phase shifts. (The scattering length will be discussed below.)

Table 4

The Convergence of the Nonadiabatic Series.

k	λ^0 δ_0	λ $\Delta\delta_0$	λ^2 $\Delta^2 \delta_0^{(1)} + \Delta^2 \delta_0^{(2)}$	δ
0	2.3482	-0.55516	-0.02477	1.7683
0.1	2.907728	0.02944	0.001865	2.9390
0.2	2.67942	0.03646	0.001758	2.7176
0.3	2.46158	0.03695	0.00111	2.4996
0.4	2.25800	0.03532	0.000235	2.2936
0.5	2.07102	0.03317	0.00104	2.1052
0.6	1.90189	0.03070	0.000872	1.9335
0.7	1.75070	0.02853	0.00084	1.7801
0.8	1.61666	0.02701	0.00076	1.6443

It must be re-emphasized that this λ series is not identical to the more traditional series strictly in powers of l. The latter may be thought of as having been derived by truncating the original set of equations (see also, Equation 4 of Reference 2) after $l = L$. That is,

$$\left[\Delta_{12} - l(l+1)\left(\frac{1}{r_1} + \frac{1}{r_2^2}\right) + \frac{2}{r_1} + \frac{2}{r_2} - M_{ll}\right] \Phi_l = \sum_{m=0}^{L} M_{lm} \Phi_m \qquad l = 0, 1, \cdots, L.$$

Assuming we could solve each of these problems exactly, we would obtain a sequence of phase shifts $\delta_{(L)}$ which would approach the exact phase shift

$$\lim_{L\to\infty} \delta_{(L)} = \delta \cdot$$

The $\delta_{(0)}$ is of course our δ_0. Beyond that Schwartz (Reference 11) has recently used his variational technique to solve for $\delta_{(1)}$.

There is, however, a somewhat more fundamental, albeit more idealized, sequence $\delta_{(L)}$ which can be defined. Assume we had the exact wave function $\Psi(r_1, r_2, \theta_{12})$. Then we could obtain the exact $\Phi_l(r_1\ r_2)$ by suitably projecting $P_l(\cos\theta_{12})$ on Ψ. We could then obtain a sequence of $\delta_{(L)}$ from the basic relation

$$\sin(\delta_{(L)} - \delta_0) = -\frac{1}{k}\sum_l \frac{2}{\sqrt{2l+1}} \iint \Phi_0^{(0)} \frac{r_2^{\,l}}{r_1^{\,l+1}} \Phi_l \, dr_1 \, dr_2 \cdot \qquad \text{(I-13)}$$

Clearly the second of these sequences of $\delta_{(L)}$ cannot be worse than the first (although the first obviously comes from a variational principle).

In Table 5 we have collated the results of Schwartz's and our calculations which bear on the latter sequence of $\delta_{(L)}$. The column marked $\Delta\delta$ is the difference $\delta_{(1)} - \delta_0$ in Schwartz's calculation.* The approximation here is the neglect of the back coupling of the higher Φ_l which distinguishes between the first and the second sequences of $\delta_{(L)}$. The analog of $\Delta\delta$ in our case is $\Delta^2\delta_0 + \Delta^2\delta_0^{(1)}$. Here the back

Table 5

Comparison of Schwartz's and Nonadiabatic Results

k	Schwartz $\Delta\delta$	Nonadiabatic $\Delta\delta_0 + \Delta^2\delta_0^{(1)}$	Schwartz $\sum_{i=2}^{\infty} \Delta^{(i)}\delta$	Nonadiabatic $\Delta^2\delta_0^{(2)}$	Schwartz δ	Nonadiabatic δ
0	0.5670	0.5644	0.0126	0.01552	1.7686	1.7683
0.1		0.02986		0.001367	2.9388	2.9390
0.2	0.0362	0.03608	0.0015	0.002135	2.7171	2.7176
0.3		0.03561		0.002447	2.4996	2.4996
0.4	0.0340	0.03306	0.0018	0.002495	2.2938	2.2936
0.5		0.03178		0.002425	2.1046	2.1052
0.6	0.0302	0.03038	0.0008	0.002291	1.9329	1.9335
0.7		0.02721		0.002160	1.7797	1.7801
0.8	0.0250	0.02571	0.0017	0.002066	1.643	1.6444

*Some time ago we requested Dr. Schwartz to use his Hylleraas variational approach to calculate δ_0 by omitting all terms depending on r_{12}. Dr. Schwartz kindly carried out these calculations which served as a check on our original zeroth order results (Reference 2). The calculations were subsequently expanded to comprise the contents of Tables 2 and 3 of Reference 11.

coupling is consistently taken into account, but we have only included two terms of a (presumably rapidly convergent) infinite series. In the column marked $\Delta^2 \delta_0^{(2)}$ we have presented only the first term of the relevant infinite series. The corresponding column of Schwartz has been obtained by subtracting his final phase shifts from $\delta_{(1)}$. If his ansatz for the wave function were exact, we could conclude that this was the contribution of all remaining multipoles,

$$\sum_{i=2}^{\infty} \Delta^{(i)} \delta \ .$$

However, the ansatz for the complete wave function contains (presumably) about the same number of parameters as that used in obtaining $\delta_{(1)}$. Therefore, it is by no means clear that projecting out Φ_1 from his Ψ will give the same accuracy as his explicitly calculated $\delta_{(1)}$.

For these reasons it can hardly be expected that there would be equality between the corresponding entries in Table 5. Nevertheless the rather wide deviation of the individual entries bespeaks of the possibility that the agreement to almost five significant figures in the final phase shifts may be somewhat coincidental. For the purposes of later discussion it should be noted that our quadrupole contribution is larger than all the remaining multipoles in Schwartz's calculation. (Thus, his results suggest a more rapid rate of convergence of the l-expansion than our own!)

Schwartz has also commented (Reference 11) on the relative angular momentum expansion in these types of problems. (The part of his scattering calculation which concerns the triplet phase shift has been given in Table 5.) The bulk of his calculation is concerned with the second order energy (for the singlet spin state):

$$E_2 = \left(\sum_n + \int dn \right) \frac{\left| \left\langle 0 \left| \frac{2}{r_{12}} \right| n \right\rangle \right|^2}{E_0 - E_n} \ . \tag{15}$$

Using the well known expansion of $2/r_{12}$ in Legendre polynomials,

$$\frac{2}{r_{12}} = 2 \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l \left(\cos \theta_{12} \right) \ ,$$

Schwartz can put Equation 15 into the form

$$E_2 = \sum_{l=0}^{\infty} E_2(l) \ ,$$

where the $E_2(l)$ can be well defined (Reference 12). With each $E_2(l)$ there is associated a wave function $\Psi_1(l)$ which, aside from the angular dependence $P_l(\cos \theta_{12})$, is a function of the two radial variable r_1 and r_2. Reduced to its bare essentials, Schwartz's argument runs as follows: if we treat each l problem variationally with the usual type of smooth polynomial trial functions, then the $l = 0$

and $l = 1$ problems can be well approximated whereas the higher l problems become increasingly difficult. The reasons for the increasing difficulty of approximation by conventional means is due to the fact that the functions $\Psi_1(l)$ have discontinuities in their second derivates coming ultimately from different analytic forms of $r_<^l / r_>^{l+1}$ in the regions $r_1 > r_2$ and $r_1 < r_2$. The discontinuities correspond to the $\Psi_1(l)$ becoming more and more sharply peaked about the line $r_1 = r_2$. On the basis that the bump itself provides the dominant contribution to the energy, Schwartz has derived the asymptotic formula for large l

$$E_2(l) \approx -\frac{45}{256}\frac{1}{l^4} \cdot \tag{16}$$

This then, defines the convergence of this specific problem rather than any inaccurate calculations for $E_2(l)$ for $l > 1$, which in general will tend to give the idea of a much more rapid convergence.*

Equation 16 applies to the specific problem of the second order energy in the singlet (space-symmetric) state; however, it is not unreasonable to assume l^{-n} characterizes the complete energy (or other physical property) in the l-expansion. Whether l^{-n} constitutes a rapidly convergent series depends on the type of problem at hand. In bound state problems where much greater experimental accuracy is in general available, it is necessary to be quite demanding in this regard. Even here, however, the convergence of Equation 16 is not in principle uncompetitive with traditional techniques. Thus, if we associate the inclusion of an additional l component with the inclusion of an additional parameter in conventional expansions, in which the use of 100 (Reference 5) and over 1000 parameters (Reference 13) has now been accomplished, a competitive 8 to 12 significant figure accuracy would be achieved. The fact that a (presently) conventional approach cannot be used in accomplishing this does not present an *a priori* objection to the rate of convergence of the l-expansion.

*Reference 11 must be read very carefully here; otherwise it may give the erroneous impression that

$$\sum_{l=2}^{4} E_2(l) \approx \frac{2}{3}\sum_{l=2}^{\infty} E_2(l) ,$$

which, if it were true, would be a more serious criticism of the convergence. What in fact is being asserted is that Schwartz's conventional calculation of

$$\sum_{l=2}^{4} E_2(l)$$

must be in error in such a way as to give a spurious rate of convergence. Nevertheless we can be quite sure that correctly

$$\sum_{l=2}^{4} E_2(l) \gtrsim (0.99)\sum_{l=2}^{\infty} E_2(l) \cdot$$

In his discussion of the extension of the relative partial wave treatment to the scattering problem, we find that Schwartz has insufficiently stressed the different physics involved. First it is clear that because of the disparity in experimental accuracy not nearly the accuracy of a bound state problem is required to correlate theory with experiment.

In order further to discuss the scattering case, it is necessary to clarify the following point. In scattering calculations $r_1 r_2$ times the wave function has a nonvanishing component

$$\lim_{r_1 \to \infty} r_1 r_2 \Psi = A \sin(kr_1 + \delta) R_{1s}(r_2) ,$$

which must be included in order to make any kind of analysis. In discussing the aspects of $r_1 r_2 \Psi$ below, we shall always disregard this nonvanishing component.

The main difference between the bound state wave function (with any kind of forces) and scattering wave functions (involving Coulomb forces) is that the bound-state wave function vanishes exponentially in all asymptotic regions of configuration space whereas the scattering wave function does not. It has been one of the primary points of the nonadiabatic theory in the decomposition of $r_1 r_2 \Psi$ in terms of $P_l(\cos\theta_{12})$, Equation I-3, that the associated Φ_l can be shown to have slowly vanishing adiabatic forms

$$\lim_{r_1 \to \infty} \Phi_l \approx - \frac{2}{\sqrt{2l+1}} \frac{\sin(kr_1 + \delta)}{r_1^{l+1}} e^{-r_2} \left(\frac{r_2^{l+2}}{l+1} + \frac{r_2^{l+1}}{l} \right) .$$

It has further been derived as one of the main results of this theory that the scattering length due to the dipole term will be diminished by an amount (Reference 7)

$$a = a(R) - \frac{9}{2} \left(\frac{1}{R} - \frac{a + a_0}{2R^2} + \cdots \right) ,$$

where $a(R)$ comes from a wave function which is more sharply cut off and hence more characteristic of a problem in a finite "sphere" of radius R. This prediction (Reference 7 and A. Temkin personal communication to C. Schwartz) was tacitly confirmed by the calculation of Schwartz (Reference 4) in which, when the variational counterpart of Φ_1 was included, his scattering length was reduced by over 5 percent. Thus, whereas the nonadiabatic theory incorporates both short-range correlations (via the convergent expansion in l) and long-range effects naturally, the Hylleraas type wave function by itself cannot practically deal with the latter. [Tables 2 and 3 of Schwartz's paper (Reference 11) include Φ_1 in the calculations of the $k = 0$ entries for $\lambda(s+p)$ as well as λ (complete).]

That a Hylleraas type wave function does not naturally describe the long-range correlations can be further brought home by reference to the paper of Ohmura and Ohmura (Reference 14.) In their

clever deduction of the singlet scattering length, these authors required the coefficient $C(\infty)$ in the adiabatic form

$$\lim_{r_1 \to \infty} \Psi = C(\infty) \frac{e^{-\gamma r_1}}{r_1} \frac{R_{1s}(r_2)}{r_2} \tag{17}$$

of the H^- wave function. Here γ is the square root of the electron affinity and being small it makes the term simulate the nonvanishing term in a scattering calculation. This form is not the analytic form of the Pekeris or Hylleraas wave functions both of which have the exponential dependence

$$\exp\left[-\frac{|E|^{1/2}}{2}(r_1 + r_2)\right],$$

where E is the total energy of the H^- ion. In order to evaluate $C(\infty)$, Ohmura and Ohmura used the 161 and 203 parameter Pekeris wave functions (Reference 5). They concluded that, whereas the wave function reproduces the adiabatic form (Equation 17) quite accurately in the region $r_1 = 10$ to 12 $(r_2 = 0)$, deviations in the variational approximations for $r_1 \geq 12$ were quite noticeable!

We shall now show that the inability of Schwartz's zero energy wave function to describe the adiabatic part of the quadrupole term can explain the difference between his triplet scattering length 1.7686, and our own 1.7683. To repeat, at zero energy Schwartz's Ψ is made to contain $\Phi_1^{(adiab)}$ but not $\Phi_2^{(adiab)}$. Using the same type analysis that we made on the dipole effect, we can write the long-range contribution of the quadrupole term as

$$a(R) - a = \lim_{k \to 0} \frac{2}{k^2 \sqrt{5}} \int_R^\infty \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^2}{r_1^3} \Phi_2 \, dr_1 \, dr_2 ,$$

$$\approx \left[\frac{15}{k^2} \int_R^\infty \frac{\sin(kr + \delta_0) \sin(kr + \delta) \, dr}{r^6}\right]_{k \to 0} ,$$

$$\approx 15\left[\frac{1}{3R^3} - \frac{1}{4}\frac{(a + a_0)}{R^4} + \cdots\right].$$

If we associate Schwartz's value with $a(R)$, a very reasonable choice of R $(R \approx 25)$ will reproduce our own value for a. Although from the experimental point of view the difference between the two numbers is completely negligible, it is worth noting that the new scattering length is outside of Schwartz's limit of error (Reference 4). We are inclined to think that the unaccounted for higher multipole may contribute an additional couple of units in the last place (see also, the $k = 0$ row of Table 4). We would extrapolate the triplet scattering length to be:

$$a_t = 1.7675 \pm .0005 .$$

A question remains at non-zero energies as to the effect of the slowly vanishing multipoles. The answer obviously depends on the accuracy in question. Schwartz claims (Reference 4) that the effects are "washed out" to his accuracy whereas our own calculation suggests that particularly the dipole contribution is not. It may very well be that our inclusion of these effects plus Schwartz's inclusion of the higher multipoles balance each other out, and that both calculations give lower bounds for the phase shifts.

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